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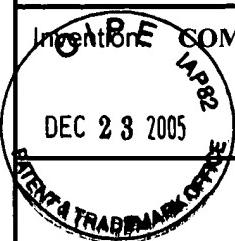
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Invention: COMPOSITION FOR ANTIREFLECTION COATING AND METHOD FOR FORMING PATTERN

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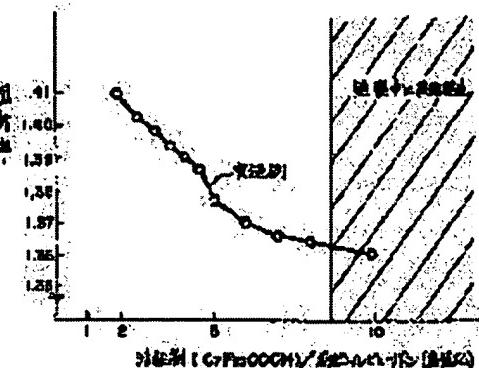
(21)Application number : 07-131096 (71)Applicant : HOECHST IND KK  
 (22)Date of filing : 01.05.1995 (72)Inventor : IWATA YUTAKA  
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## (54) COMPOSITION FOR ANTIREFLECTION COATING

### (57)Abstract:

**PURPOSE:** To obtain a compsn. for forming a high quality anti-interference film on a photoresist film by incorporating perfluoro alkylcarboxylic acid, org. amine, polyvinylpyrrolidone and water.

**CONSTITUTION:** This compsn. contains perfluoroalkylcarboxylic acid, org. amine, polyvinylpyrrolidone and water. The perfluoroalkylcarboxylic acid is a compd. represented by the formula  $C_nF_{2n+1}COOH$  [where (n) is 5–10] and  $C_7F_{15}COOH$  is preferably used. The perfluoroalkylcarboxylic acid is used as an activator and dissolves under coexistence of a basic substance. The basic substance used here is the org. amine and alkanolamine, especially monoethanolamine is preferably used. By the combination of the components, a lower refractive index is ensured and a slightly soluble layer is not formed on a resist.



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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The constituent for antireflection coating characterized by containing a perphloro alkyl carboxylic acid, an organic amine, a polyvinyl pyrrolidone, and water.

[Claim 2] Said perphloro alkyl carboxylic acid is general formula  $C_nF_{2n+1}COOH$ . ( $n=5-10$ )

The constituent for antireflection coating according to claim 1 which comes out and is characterized by being the compound expressed.

[Claim 3] The constituent for antireflection coating according to claim 1 characterized by said organic amine being alkanolamine.

[Claim 4] The constituent for antireflection coating according to claim 1 characterized by for said perphloro alkyl carboxylic acid being  $C_7F_{15}COOH$ , and said organic amine being monoethanolamine.

[Claim 5] It is the constituent for antireflection coating according to claim 1 with which molecular weight of said polyvinyl pyrrolidone is characterized by 1000-20000, and being 2000-10000 preferably.

[Claim 6] The constituent for antireflection coating according to claim 1 or 5 characterized by the amount of vinyl-pyrrolidone monomers contained in said polyvinyl pyrrolidone being 100 ppm or less.

[Claim 7] The rate of said perphloro alkyl carboxylic acid and polyvinyl pyrrolidone is a constituent for antireflection coating according to claim 1 characterized by being the perphloro alkyl carboxylic acid 4 - 8 weight sections to the polyvinyl-pyrrolidone 1 weight section.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] In case this invention performs pattern formation with a photolithography technique in detail about the constituent for antireflection coating using a photoresist, it relates to the constituent for antireflection coating for forming the interference prevention film for preventing lowering (fluctuation of pattern dimension width of face) of the pattern dimensional accuracy brought about by interfering with the reflected light from a substrate in the photoresist film on the photoresist film.

[0002]

[Description of the Prior Art] After manufacture of a semiconductor device forming the photoresist film on substrates, such as a silicon wafer, generally and irradiating an activity beam of light selectively at this, the lithography technique which performs a development and forms the pattern of a photoresist on a substrate is applied.

[0003] By the way, as touched previously, when an activity beam of light is irradiated selectively at the photoresist film, changing pattern dimension width of face for interferential action is known. For this reason, the examination for making fluctuation of the aforementioned pattern dimension width of face as small as possible is made here and there. If the some are raised, (1) JP,5-188598,A, (2) JP,6-148896,A, etc. can be illustrated.

[0004] The above (1) is a constituent for antireflection coating formed on the photoresist film, and what is constituted with a water-soluble polymer binder and water-soluble fluorocarbon compounds (quaternary ammonium salt of a perphloro carboxylic acid and a perphloro sulfonic acid etc.) is indicated. Moreover, if the transparent membrane of 1.401 is obtained for a refractive index and it applies to a photolithography process actually with this constituent, as compared with the case where there is no antireflection coating film, it is supposed that the variation in the sensibility by photoresist thickness fluctuation will decrease. And the variation in this sensibility is based on the multiplex cross protection of the light in the inside of the resist film, and the ideal refractive index of an antireflection film supposes that it is  $\sqrt{N_{\text{resist}}} = 1.28-1.30$ .

[0005] Moreover, the resist pattern which was excellent in pattern dimensional accuracy is formed by preparing the coating liquid for resists which contained the water-soluble film formation component and the fluorochemical surfactant above (2), and the interference prevention film which consists of the coating liquid in a resist front face. As a water-soluble film formation component here, in the molecule, it is an acrylic-acid system polymer, a polyvinyl pyrrolidone, etc. which do not have a hydroxyl group and which are a water-soluble polymer, and, on the other hand, a perphloro carboxylic acid, a perphloro sulfonic acid, or each quaternary ammonium salt is illustrated as a fluorochemical surfactant.

[0006]

[Problem(s) to be Solved by the Invention] However, above (1), when the antireflection film is formed on a resist, the development remainder (insolubilization layer) may occur in the management of a resist pattern after development. The novolak resin and the naphthoquinone azide compound this phenomenon

of whose is a resist component are considered because a lifting surface part becomes a developer with insolubility about an interaction by existence of quarternary ammonium salt. Moreover, the actual condition is still far from an ideal refractive index. Furthermore, above (2), only by RfCOOH, it is insoluble (it dissolves only after a base exists), and, in the case of RfCOOM and RfSO<sub>3</sub>M (M is the fourth class ammonium compound), water has the fault of forming a refractory-ized layer in a resist front face.

[0007] It is in the object of this invention offering the constituent for antireflection coating for canceling the above faults and forming the good interference prevention film on the photoresist film.

[0008]

[Means for Solving the Problem] As a result of having examined antireflection coating liquid from various include angles, when this invention persons used the constituent for coatings which combined a perphloro alkyl carboxylic acid, an organic amine, a polyvinyl pyrrolidone, and water, the refractory-ized layer could form the good acid-resisting layer not becoming on the photoresist pattern, the refractive index further more near ideal value was obtained, and it found out that the sensibility (variation in a dimension) by resist thickness fluctuation could be reduced. This invention is made based on this.

[0009] It sets to the constituent for antireflection coating and (2) above (1) which are characterized by including (1) perphloro alkyl carboxylic acid, an organic amine, a polyvinyl pyrrolidone, and water according to this invention, and a perphloro alkyl carboxylic acid is general formula C<sub>n</sub>F<sub>2n+1</sub>COOH. (n=5-10)

In the constituent for antireflection coating and (3) above (1) which come out and are characterized by being the compound expressed, constituent \*\* for antireflection coating characterized by an organic amine being alkanolamine is offered.

[0010] Moreover, according to this invention, in (4) above (1), the constituent for antireflection coating characterized by for a perphloro alkyl carboxylic acid being C<sub>7</sub>F<sub>15</sub>COOH, and said organic amine being monoethanolamine is offered.

[0011] Moreover, according to this invention, in (5) above (1), constituent \*\* for antireflection coating characterized by the amount of vinyl-pyrrolidone monomers by which the molecular weight of a polyvinyl pyrrolidone is contained in a polyvinyl pyrrolidone in 1000-20000, the constituent for antireflection coating with which it is characterized by being 2000-10000 preferably, (6) above (1), or (5) being 100 ppm or less is offered.

[0012] Furthermore, according to this invention, in (7) above (1), the constituent for antireflection coating with which, as for the rate of a perphloro alkyl carboxylic acid and a polyvinyl pyrrolidone, a perphloro alkyl carboxylic acid is characterized by being 4 - 8 weight section to the polyvinyl-pyrrolidone 1 weight section is offered.

[0013] Hereafter, this invention is further explained to a detail. The perfluoroalkyl carboxylic acid used by this invention is general formula C<sub>n</sub>F<sub>2n+1</sub>COOH preferably. (n=5-10)

It comes out, and it is expressed and especially the activity especially of C<sub>7</sub>F<sub>15</sub>COOH is desirable especially. This perphloro alkyl carboxylic acid is used as an activator, and although it is insoluble in water, there is a property which will be dissolved if the alkali lives together.

[0014] A polyvinyl pyrrolidone is used as an aqueous polymer binder. It is raised good [ the paint film engine performance at the time of (i) spin spreading ] as a required property in a water-soluble common polymer binder, that compatibility with the (ii) fluorochemical surfactant is good, that the solubility to the water after elevated-temperature (iii) BEKU processing (about 150-160 degrees C) is good, that not having the absorption to the light of the wavelength which is 2300nm and (iv) (v) refractive index are low, etc.

[0015] In these, the polyvinyl pyrrolidone of low molecular weight (Mw=1000-20000) is good in the above (ii) and (iii). Furthermore, when PAA (polyacrylic acid) was used as a water-soluble polymer about (ii), the weight ratio of the amount of an activator of this polymer and activator (perphloro alkyl carboxylic acid) increased more than 1:2.5 and a polyvinyl pyrrolidone is used instead of PAA to that in which precipitate comes ( drawing 2 ) to be accepted into a paint film, a paint film with that ratio

homogeneous to about 1:8 comes (drawing 1) to be obtained.

[0016] the PORIPI nil pyrrolidone used by this invention -- desirable -- molecular weight 1000-20000 -- it is the thing of 2000-10000 still more preferably. If molecular weight is smaller than 1000, stable membranous quality will be hard to be obtained, and if larger than 20000, the inclination which becomes poor [ the cobwebbing at the time of a spin coat or a paint film ] will be seen. Since a refractive index becomes low, it is so advantageous that the rate that it is measured like drawing 1 and an activator occupies is large. [ of the relation between a perphloro alkyl carboxylic acid (activator) / polyvinyl-pyrrolidone ratio, and a refractive index ]

[0017] Although a perphloro alkyl carboxylic acid dissolves under coexistence of an alkali as above-mentioned, the alkali used by this invention is an organic amine, and its activity of alkanolamine, especially monoethanolamine is desirable especially. Therefore, in this invention, with the combination of a perphloro alkyl carboxylic acid, polyvinylpyrrolidone, an organic amine, and water, a lower refractive index is obtained and formation of a refractory-ized layer does not take place on a resist. A perphloro alkyl carboxylic acid and an organic amine can adopt the presentation ratio of arbitration. The same is said of water. Water is desirable and pure water (ion exchange water) is used.

[0018]

[Example] Next, it explains concretely to give an example and the example of a comparison and carry out this invention.

[0019] It agitates until it puts 163g of ion exchange water, and 2-aminoethanol 2.5g into example 1 beaker and becomes homogeneity. What added polyvinyl-pyrrolidone 3.0g of molecular weight 3,000 and 5.4g (trade name FC-26 / 3 M company make, or EF-201/TOKEMU products company make) of perphloro carboxylic acids to this, and was dissolved in it is filtered, and it considers as a sample. Similarly, the sample which changed the addition of a perphloro carboxylic acid is prepared. Each sample is adjusted so that the thickness may become 650A on a silicon wafer.

[0020] The prepared sample is applied on a silicon wafer, respectively, and while observing this applied film under a microscope, thickness and a refractive index are measured in ERIPURI meter (made in Rudolf AEL-4).

[0021] Subsequently, on a silicon substrate, spin spreading of positive type photoresist AZ-7700 is carried out so that thickness may be set to about 1 micrometer. Then, on this resist film, spin spreading of the sample produced above was carried out, and 90 degrees C and baking for 90 seconds were performed on the hot plate. i line stay par performed pattern exposure after that, and PEB processing for 90 seconds was performed at 120 more degrees C. After developing negatives finally using a TMAH (tetramethylammonium hydroxide)2.38% water solution, the resist pattern front face was observed in SEM. The condition of the refractory-ized layer on a resist pattern was judged as compared with the resist pattern which has not applied this sample. The refractive index of each sample was shown in drawing 1.

[0022] Although the film with a perphloro carboxylic acid homogeneous [ about eight ] was obtained to the polyvinyl pyrrolidone 1 (weight ratio) as a result of the observation under a microscope, when the addition of a perphloro carboxylic acid was increased further, the crystallization object's object was generated in the film. Moreover, although it applied on the resist and patterning was carried out, the beautiful pattern which a phenomenon like the film remainder is not accepted, either, does not have generating of the refractory-ized layer on the front face of a resist, either, and does not have the same defect as the time of the pattern formation of only a resist about which sample, either was formed as a result of SEM observation. (The example and the example of a comparison were hereafter performed by the same actuation as an example 1.)

[0023] Example 2 Polyvinyl pyrrolidone (molecular weight: 3000) 3.0g C7F15COOH 18.0g 2-aminoethanol 2.5g Ion exchange water The constituent for antireflection coating which consists of 400g was prepared. The refractive index of this thing was 1.37. Moreover, at the sample which changed the molecular weight of a polyvinyl pyrrolidone in the above-mentioned presentation, it is 1Mw. : 3000 Spreading film fitness, 2Mw : 9000 Spreading film fitness, 3Mw:45000 The result of \*\* which spreading nonuniformity tends to generate was obtained.

[0024] When the molecular weight of a polyvinyl pyrrolidone used the thing of 9000 in the presentation of example 3 example 2, the fluorine system activator was advantageous.

[0025] When the water solubility of an example 4 organic amine and the salt by the combination of a fluorine system activator was investigated, in alkylamine, aromatic amine, ethanolamine, and water, ethanolamine was good, and the effect of 2-aminoethanol on a refractive index was good few especially.

[0026] Example 1 of a comparison Polyacrylic acid 3.0g C7F15COOH 5.4g Tetramethylammonium hydroxide (5% water solution) 24.0g Ion exchange water The constituent for antireflection coating which consists of 160.0g was prepared. The refractive index of this thing is 1.41 and formed the refractory-sized layer on the resist front face.

[0027] Example 2 of a comparison Polyacrylic acid 3.0g C7F15COOH 5.4g 2-aminoethanol 1.5g Ion exchange water The constituent for antireflection coating which consists of 160.0g was prepared. The refractive index of this thing was 1.43, and although a refractory-sized layer does not happen and it will stage formation on a refractive index on a resist front face, it accepted.

[0028] Example 3 of a comparison Polyacrylic acid 3.0g C7F15COOH 5.4-30.0g 2-aminoethanol 1.5g Ion exchange water Since it was proper, the becoming constituent for antireflection coating was prepared. Although a refractive index falls with loading of a fluorine system activator as the broken line showed the refractive index of this thing to drawing 2, a lot of particles have occurred in the film. In addition, formation of the refractory-sized layer on the front face of a resist did not take place.

[0029] Example 4 of a comparison Polyacrylic acid 3.0g C8F15SO<sub>3</sub>H 5.4-30.0g 2-aminoethanol 2.5g Ion exchange water Since it was proper, the becoming constituent for antireflection coating was prepared. Although a refractive index falls with loading of a fluorine system activator as the continuous line showed the refractive index of this thing to drawing 2, a lot of particles have occurred in the film. In addition, formation of the refractory-sized layer on the front face of a resist did not take place.

[0030] Example 5 of a comparison Polyvinyl pyrrolidone (molecular weight: 3000) 3.0g C7F15COOH 18.0g Aqueous ammonia (30wt%) 2.1g Ion exchange water The constituent for antireflection coating which consists of 400.0g was prepared. Although the refractive index of this thing was 1.362, formation of the refractory-sized layer on the front face of a resist was checked.

[0031]

[Effect of the Invention] According to this invention, the refractory-sized stratification is reduced and the constituent for antireflection coating with a low refractive index is obtained.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] The graph showing the relation between the mixed rate of an activator (perphloro alkyl carboxylic acid) and polyvinyl HIRORIDON, and a refractive index.

[Drawing 2] The graph showing the relation between the mixed rate of an activator (the fluorine compound of a carboxylic-acid system, or fluorine compound of a sulfonic-acid system), and polyacrylic acid, and a refractive index.

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[Translation done.]